Metal Halide Nanostructures: Synthesis and Energy Storage Properties

Synopsis in Candidature for the Degree of

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Submitted by

Mr. Hesham Gaber Saleh Wasel

Under the guidance of

Dr. Shyam K. Gore

Department of Physics

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1. Introduction

The development of sustainable energy resources is critical for living species, not only to meet fundamental requirements but also to meet future demands. The increasing energy problem in recent decades has been caused by the rising cost of fossil fuels, as well as their depletion, which has a negative influence on issues such as pollution and global warming [1, 2]. Electrochemical storage systems have the potential to solve all of these problems. The most promising electrical energy storage systems are ordinary capacitors, electrochemical capacitors (ECs), batteries, and fuel cells, among others, which transform chemical energy into electrical energy. ECs, which is also known as supercapacitors or ultracapacitors, serve as a bridge role for energy/power between batteries and fuel cells, with a large energy-power storage capacity [3] that have garnered significant interest in several industries, including as hybrid electric cars and smart portable gadgets, during the last few decades [4].

There are two distinct categories of supercapacitors; symmetric supercapacitors and asymmetric supercapacitors. A symmetric supercapacitor consists of either an electrostatic double-layer capacitor or a pseudocapacitor. On the other hand, asymmetric supercapacitors possess hybrid supercapacitor characteristics. A symmetric supercapacitor employs electrodes with same properties, while an asymmetric supercapacitor utilizes electrodes with distinct characteristics. One display mostly electrostatic capacitance, while the other demonstrates electrochemical capacitance. ECs can be categorized into two main mechanisms; (a)

electrochemical double-layer capacitors (EDLCs), where the dominant mechanism is diffusion and the reaction occurs at the interface between the electrode and electrolyte, and (b) Faradaic supercapacitors (FS) or pseudo-capacitors, where redox reactions are significant due to the presence of multiple redox states. The superior performance of pseudocapacitor materials, as opposed to EDLC materials, in supercapacitors find different avenues for researcg [5, 6].

Metal halide materials may be produced with a highly ordered crystal structure, exhibiting intriguing mechanical, optical, and electrical characteristics [7, 8]. Notably, the metal halides have garnered the interest of academics and researchers in energy storage appliances [9]. The charge carriers, such as electrons and ions in metal halides are acceleratedthrough the ambipolar charge transport mechanism inside the crystal lattice plane [10]. As a result, the material has exceptional conductivity despite its organic nature. The choice of metal ions plays a crucial role in the transportation of ions at the interface of nanocrystals (NCs). Additionally, the movement of these ions in the active layer of low-dimensional metal halide materials may have a significant impact on surface polarisation and perhaps increase the total capacitance [11]. Determining the crystal structures and chemical composition of these metal halides may heavily rely on identifying suitable metals, halogens, and organic cations. Various metal halide nanostructures were developed by choosing the size of the organic cations, halogens, and regularizing metal cations in the past [12-14].

New classe of lead-free halide materials were developed to replace lead (Pb) with elements like antimony (Sb), bismuth (Bi), germanium (Ge), indium (In), and tin (Sn) etc., of which bismuth has garnered significant interest because to its favourable band gap, strong carrier mobility, and other desired features, which may be attributed to its similar ionic radius and electronic structure [15, 16].

The Bi-based materials exhibit significantly enhanced resistance to degradation in the presence of air and moisture as compared to the Pb-based materials which is attributed to the distinct cubic phase of the perovskite structure and the high dielectric constant of Bi (III), which effectively shields charged defects present in the material. There is a literature scarcity on supercapacitors made from metal halides Primarily, energy storage devices use Bi-based compounds such as Bi_2O_3 nanotubes/nanobelts, Bi_2S_3/functionalized graphene nanosheet, and bismuth chalcogenides, namely Bi_2X_3 (X = O, Se, S, Te) [16-19]. Nevertheless, the literature lacks a comprehensive understanding of the impact of ion interaction on the composition of lead-free bismuth-based perovskite $A_3Bi_2X_9$ (where A is metal and X might represent Cl^-, Br^-, I^-, and F^-). The main challenge in the commercialization of metal halide perovskite technology is the development of simplified, cost-effective, non-toxic, and highly repeatable methods for synthesizing these materials. This is crucial for successfully transitioning this technology from the laboratory to mass production [20, 21].

2. Literature review

In the last few years, there has been a significant emphasis on conducting research to create electrode materials using abundant, cost-effective, and environmentally friendly metal halides. These materials, including NiF_2, $NiCl_2$, and $NiBr_2$ are being explored in various morphologies. This research is being conducted alongside investigations into oxides, carbides, and hydroxides, as the cost of electrode materials such as RuO_2 and platinum is relatively high and limited to niche markets in the electronics industry [22]. Nickel halide was used as a raw material to generate photoelectric materials or organic chemical reaction catalyst [23]. Different metal halides like BiOI [24], BiOCl [25], NiF_2 [26] $NiCl_2$ [27], $CuCl_2$ [28] etc., were prepared and used for SC application. Shinde *et al*., obtained binder-free NiF_2 nanorods on nickel-foam (NiF) by hydrothermal route which in later stage was envisaged as electrode material for supercapacitor application. A symmetric supercapattery device fabricated using NiF_2@NiF nanorod arrays revealed 51 F cm^{-2} ASC at 0.25 mA cm^{-2} current density with 94% cycling stability [27] . There are very limited reports available on the room-temperature growth and electrochemical energy storage applications of $NiCl_2$@NiF electrode materials. Another studies, Tian *et al*., synthesized oxygen vacancy rich BiOBr nanosheets by a facile hydrogenation process that, in addition to reasonable cycling stability, displayed 689 F g^{-1} SC at a current density of 0.5 A g^{-1} [29]. As far as for nickel (Ⅱ) halides MX_2 (M = transition metal, X = F, CI, Br and I) concern, most of the investigations have been

emphasized on the catalytic, magnetic, and photoelectric transforming applications and research on electrochemical energy storage application is sporadic.

Notably, all of the scenarios presented above include cost-effective self-developed metal halide nanostructures with a variety of morphologies, series resistances, and large surface areas, as well as a detailed chemical synthesis method for electrochemical energy storage applications.

3. Objectives of the study

This thesis aims at achieving the following objectives;

1. To synthesize efficient, inexpensive, novel metal-halides and transition metal-doped metal halides for supercapacitor technology using a soft chemical methods.
2. To characterize them for their structure, morphology and phase purity by using various measurements like XRD, SEM, XPS, FTIR, HR-TEM and Raman spectrometer techniques.
3. To obtain a high specific capacitance, cyclic life, and excellent rate capability.
4. Fabrications of symmetric and asymmetric supercapacitors.
5. Efforts will be made to understand obtained results of metal halide and transition-metal doped metal halide nanostructures on supercapacitor performance computationally.
6. To compare these results with data reported previously.
7. To report obtained results with analyses and conclusions in high indexed research journals.
8. To frame thesis accordingly based on the data produced and work published.

4. Synthesis Methods

4.1 Hydrothermal method

In hydrothermal synthesis method, synthesis of materials in various nanostructures on conducting and non-conducting substrate surfaces at temperature from 50 to 200 ^{o}C is taking place. In this process, there is the teflon-lined stainless-steel autoclave which possesses the base current collector in the presence of suitable solvent at an annealing temperature less than 200 ^{o}C for a few h. There is the production of the material on the host metallic substrate as a by-product, and this is because of reaction bath pressure and temperature. Therefore, this self-grown synthesis method provides following benefits; a) a good lattice match between the base conductive material and the product material, b) production of different morphologies with different surface areas, which increases the overall redox reaction rate and thus electrochemical performance. c) Fast and easy charge transportation.

Fig 1. Hydrothermal autoclave reactor image.

4.2 Successive ionic layer adsorption and reaction (SILAR)

Successive ionic layer adsorption and reaction i.e. SILAR method is economical, highly feasible for large area deposition. For the deposition of material in thin film, a well-cleaned glass substrate need to be immersed in the cationic precursor solution, causing cations to be adsorbed on the surface of the glass substrate. This substrate should then be immersed in an ample amount of double distilled water to prevent homogenous precipitation. The substrate would then be immersed in the anionic precursor solution. Anions reacted with the adsorbed cations on the glass substrate. The substrate was then immersed in double-distilled water.

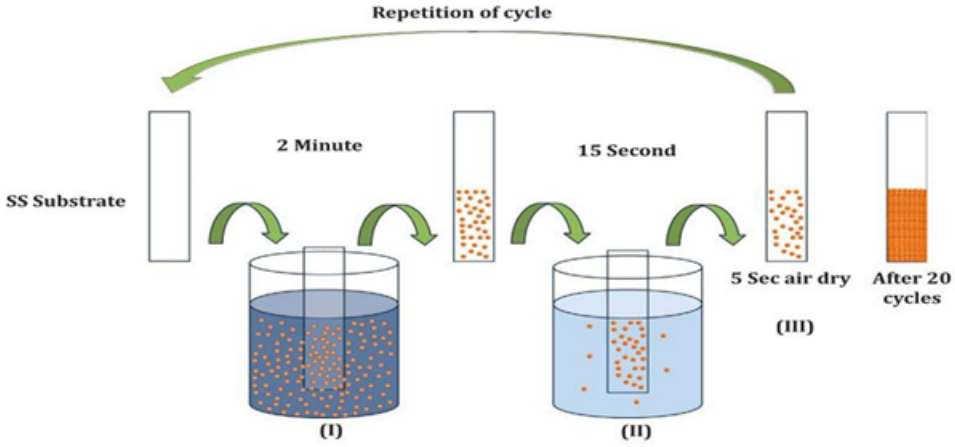

Fig 2. Steps involved in SILAR

4.3 Chemical bath deposition

The metal halide electrodes will be prepared by adjusting CBD preparative parameters, such as deposition temperature, time, pH, complexing agent etc., as shown in Fig. 1. The metal oxide films were deposited from the solution containing precursor by using different complexing agent.

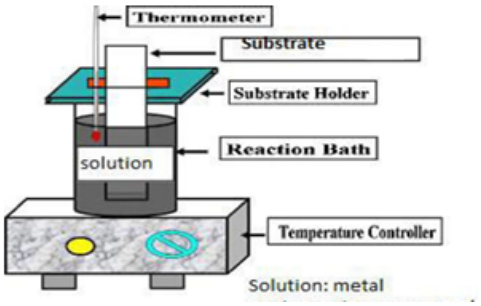

Fig 3. Diagram of chemical bath deposition method.

4.4 Electrodeposition

Electrodeposition is a well-known conventional surface modification technique to improve the surface characteristics, both decorative and functional, of a wide variety of materials. It is a versatile and inexpensive technique that can be performed at mild temperatures (≤ 00°C) which will minimize inter diffusion of materials in the case of a multi layered thin-film preparation. The film thickness can be controlled by monitoring the amount of charge delivered, whereas the deposition rate can be followed by the variation of the current with time, and the schematic arrangement of the electrodeposition arrangement, which is shown in Fig. 2. This is based on controlled current or controlled potential electrochemical deposition on an electrode from a solution containing the appropriate species. Therefore, the electrodeposition method is frequently used for the deposition of a wide range of compounds, including metals, semiconductors, mixed metal oxides, and magnetic structure.

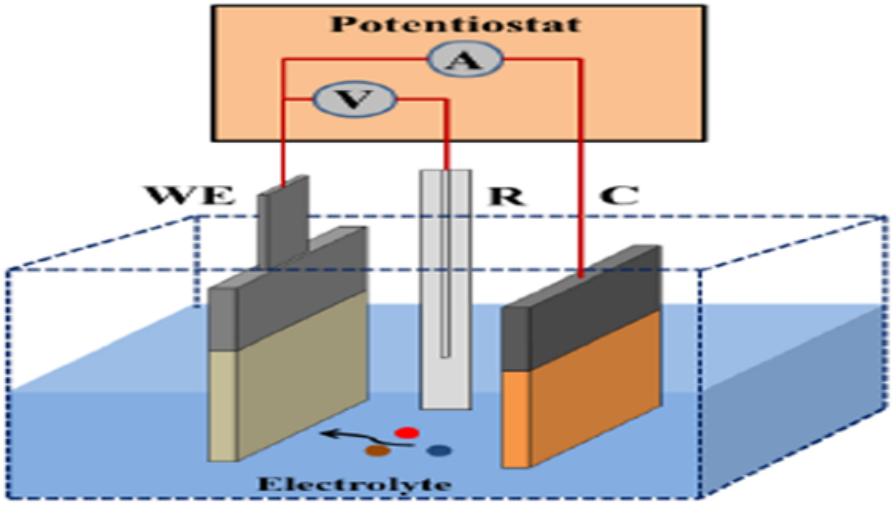

Fig 4. Electrodeposition method sketch.

5. Characterizations

A concise account of the instruments and techniques used for acknowledgement of structural, morphological, electrical and electrochemical supercapacitor properties of the as-deposited metal halide and transition metal doped metal halide electrode materials.

5.1 Structural analysis X-ray diffraction technique is a one of the influential, renowned and

most appropriate techniques for structural revelation of materials prepared in the form of films or powders.

5.2 Raman Spectroscopy Raman spectroscopy is a spectroscopic technique used to observe vibration, rotational, and other low-frequency modes in a system.

5.3 Fourier transform infrared spectroscopy FT-IR spectroscopy is a tool for investigation of the various chemical groups present in the sample material.

5.4 Morphology monitoring Field-emission scanning electron microscopy will be used for investigating the surface morphology of the as-prepared composite electrodes.

5.5 High resolution transmission electron microscopy HR-TEM, one of most powerful techniques, is used in the characterization of nanostructuress. It has capacity to inspect the constitutional characteristics of nanocomposites such as grain shape and size, crystallinity and chemical variations at a nanometer scale resolution.

5.6 Electrochemical workstation

The as-prepared metal halide and transition metal doped metal halide nanostructures will be used to prepare electrodes for supercapacitor applications. The IVIUM electrochemical workstation will be used to measure Cyclic-Voltammetry (CV), Galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). Also, Mott-Schottky measurements will be carried out for confirmation the type of conductivity and also for knowing the flat band potential of the composite nanostructured electrodes.

6. Plausible outcomes

• Synthesis of metal halide and transition metal doped metal halide will be carried at an initial stage.

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The electrochemical measurements of the as-prepared metal halide and transition metal doped metal halide nanostructures will be measured and studied in different electrolytes such as KOH, H_2SO_4, NaOH, KCL, etc.

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The symmetric and asymmetric devices will be built to designed and their electrochemical properties will be investigated.

• Based on results obtained and analysis performed, writing and publishing research articles, reviews and patents will be undertaken.

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Research scholar

Hesham Jaber Saleh Wasel

Research Guide

Dr. Shyam K. Gore
Department of Physics
Shivaji Mahavidyalaya, Udgir 413 517
Phone: + 919422879596